U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-282 367

Role of Physico-Chemical Properties of Aroclors 1016 and 1242 in Determining Their Fate and Transport in Aquatic Environments

Environmental Research Lab, Athens, Ga.

1978

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3.
EPA-600/J-78-014	JOURNAL ARTICLE	PB 282 367

4. TITLE AND SUBTITLE	5. REPORT DATE
Role of Physico-Chemical Properties of Aroclors 1016 and 1242 in Determining Their Fate and Transport in Aquatic Environments	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Doris F. Paris, William C. Steen, and George L. Baughman	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory U.S. Environmental Protection Agency College Station Road Athens, GA 30605	10. PROGRAM ELEMENT NO. 1HE775 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency-Athens, GA Environmental Research Laboratory College Station Road Athens, GA 30605	13. TYPE OF REPORT AND PERIOD COVERED Journal Article 14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES
Published in Chemosphere 7(4):319-325, 1978
Contact: D.F. Paris, 8-250-3469

16. ABSTRACT

Water solubilities of Aroclors 1016 and 1242 and the sorption and volatilization characteristics of the two polychlorinated biphenyls in aqueous solutions were studied. Water solubilities of Aroclors 1016 and 1242 were 0.42(±0.08) and 0.34(±0.06) mg/1, respectively. Partition coefficients for both Aroclors to bacteria and seston ranged from 1.2 to 8.3 x 10^3. Volatilization studies indicate that the rate coefficient for loss of Aroclor 1016 or 1242 from water is about one-fourth the oxygen reaeration rate coefficient for the same system.

8300

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Volatility Solubility Sorption Water Contaminant	Aroclor 1016 Aroclor 1242	07C 07D 11H

REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	9
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	A02-A01

EPA-600/J-78-014
JOURNAL ARTICLE

Chemosphere No. 4, pp 319 - 325, 1978. 0045-6535/78/0401-0319$02.00/0
© Pergamon Press Ltd. Printed in Great Britain.

ROLE OF PHYSICO-CHEMICAL PROPERTIES OF AROCLORS 1016 AND 1242 IN DETERMINING THEIR FATE AND TRANSPORT IN AQUATIC ENVIRONMENTS

Doris F. Paris, William C. Steen, and George L. Baughman
Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, Georgia 30605, U.S.A.

(Received in USA 13 January 1978; received in UK for publication 6 April 1978)

INTRODUCTION

Complex interrelationships between the properties of a chemical and the characteristics of its environment govern the fate of materials in natural aquatic systems. An understanding of these relationships is important to predicting the rates of transport of environmental pollutants. To this end, the physico-chemical properties of Aroclors 1016 and 1242, two polychlorinated biphenyls (PCB's), were measured. PCB's, identified as major environmental contaminants since the early 1970's, have been the subject of several review articles[1,2] that describe the prevalence and persistence of these ubiquitous materials.

MATERIALS AND METHODS

Aroclor 1016 (lot #KB-06-756) and Aroclor 1242 (lot #AK-255) were used as received without further purification. Water solutions of the Aroclors were prepared by equilibration with the vapor phase and by direct addition of the PCB's to the water. Natural waters were collected from ponds within a 10-mile radius of the Athens laboratory; bacteria were isolated from the same ponds.

Gas-liquid chromatography

All quantitative determinations were made using a Tracor MT-220 gas-liquid chromatograph equipped with a Nickel-63 high temperature electron capture detector. The Aroclors were extracted from aqueous solutions with 2, 2,4-trimethylpentane (isooctane) and no sample clean-up was needed. A glass column (2 m x 4 mm ID) containing 80-100 mesh Gas Chrom Q coated with 3% SE-30 (Supelco) was used for separation of the mixtures into 12 to 15 distinct fractions. The nitrogen carrier gas flow was 70 ml/min.; operating temperatures for inlet port, detector, and column oven were 225°C, 275°C, and 195°C, respectively.

Response factors were determined according to the procedures of Webb and McCall[3]. Aroclor quantities were determined by measuring each peak height, multiplying the height value by the response factor for that peak, and summing the amounts from individual peaks. Recoveries from spiked water samples ranged from 92 to 96%.

Water saturation studies

Lower halves of 2-liter, glass-stoppered bottles were coated with 2 ml of acetone containing different amounts (0.1-100 mg/ml) of each Aroclor. Coating

of the bottles was continued until the acetone evaporated. Two liters of sterile distilled water were added, and solutions were stirred at room temperature (25 ± 1°C) on magnetic stirrers for 2 weeks followed by 2 weeks of quiescence. The experiment was triplicated. Samples were taken at 24, 72, and 96 h followed by weekly sampling. Samples were centrifuged in closed tubes for 1 h at 18,000 rpm in a Sorvall RC-2 centrifuge at room temperature followed by glc analysis of the organic solvent extract of the supernatant.

Sorption Studies

Bacteria were incubated for 24 hours at 28°C in nutrient broth, harvested by centrifugation, and washed three times in sterile dilution water prior to inoculation in test medium. Seston was collected by centrifugation. Dry weights of bacteria and seston were determined by oven drying at 90°C.

The sorptive properties of the bacteria and seston were determined by suspending the cells or seston in distilled water solutions of Aroclor (0.05 to 0.3 mg/l) on a gyratory shaker at 28°C. Seston concentrations ranged from 50 to 300 mg/l (dry wt.); bacteria concentrations ranged from 50 to 500 mg/l (dry wt.). Sorption equilibrium was reached within 30 minutes in all systems. At each sampling, the aqueous suspension of seston or bacteria was centrifuged and the Aroclor remaining in the supernatant measured by glc analysis of the organic solvent extract. Mass balance determinations of early samples indicated this procedure to be satisfactory.

To determine partition coefficients for n-octanol - water, Aroclor 1016 or 1242 was dissolved in n-octanol (saturated with water) and the solution was shaken with water for at least 2 min. After separation of the two layers, the concentration of Aroclor in each layer was determined. The Aroclors were also dissolved in water, the solution shaken with n-octanol, and the concentration of Aroclor in each layer determined.

Volatilization

One liter of water containing Aroclor 1016 or 1242 was added to each of six 2-liter beakers. The aqueous solutions were sparged with nitrogen until dissolved oxygen was 1 mg/l or less. Contents of beakers 1 and 2 were stirred to create a 2-cm vortex; beakers 3 and 4, 4-cm vortex; and beakers 5 and 6, 9-cm vortex. Oxygen and Aroclor concentrations were measured every 5 min. and every 15 min., respectively, for 240 min. using a dissolved oxygen meter and a gas chromatograph. Water temperature was 23°C.

Henry's law constant was determined by measuring the partial pressure of Aroclors 1016 and 1242 and its mole fraction in water. Saturated and more dilute solutions (1:10, 1:100, and 1:1,000) were used. Systems were equilibrated for at least 96 h in a controlled temperature shaker (25°C) before sampling.

All data are reported with standard deviation. Solubility and Henry's law constant values are means of 16 determinations; partition coefficients, means of 6 determinations; and ratios of oxygen reaeration coefficients to Aroclor volatilization rate coefficients, means of 8 determinations.

RESULTS AND DISCUSSION

Water solubility studies

The true solubility of mixtures, like Aroclors 1016 and 1242, is undefined because water concentration at equilibrium is controlled by partitioning of the

individual components between water and the mixture itself. The apparant solubility of individual components of a mixture is described by

$$K = \frac{C_A}{C_W} \quad (1)$$

where: K = partition coefficient of a component between water and mixture.

C_A = concentration of the component in the mixture at equilibrium.

C_W = concentration of the component in water at equilibrium.

Consequently, the apparent solubility of the mixture is given by KC_W. Partition coefficients for 2,2'-dichlorobiphenyl and 3,4,2'-trichlorobiphenyl in Aroclor 1242 were calculated from equation 1 and found to be 1.7×10^5 and 2.3×10^6, respectively. As expected, the early eluting components having lower partition coefficients contributed proportionately more to the total water concentration at saturation.

Saturation of the aqueous solutions of Aroclors 1242 and 1016 occurred in less than 1 week with the apparent solubility being 0.34 (± 0.06) and 0.42 (± 0.08) mg/l, respectively. To our knowledge, the determined water solubility of Aroclor 1016 has not been reported. However, Tucker et al.[4] have estimated it to be in the range of 0.22-0.250 mg/l. Their estimate is based on the fact that Aroclor 1016 contains more of the less highly chlorinated isomers than does Aroclor 1242. Water solubilities of 1242 have been reported to be 0.20 and 0.24 mg/l by Nisbet and Sarofim[5] and Mackay and Wolkoff[6], respectively. Factors contributing to the difference could be different "lots" of Aroclor 1242, volatilization of the material from water, and different methods of determination.

Introduction of Aroclors into water by equilibration with the vapor phase resulted in slightly higher average water concentrations than those determined by direct addition of the Aroclors. The values are within experimental error; the major difference being that the concentrations of the early eluting components are a little greater when PCB's are introduced through the vapor phase.

Sorption studies

Hydrophobic compounds, like DDT, methoxychlor, toxaphene, or PCB's, can sorb to seston or microorganisms in aquatic systems[7-13].

For low solution concentrations, sorption of a compound to seston may often be adequately described by a partition coefficient (equation 1).

Experimentally measured partition coefficients are listed in Table 1. Values of the partition coefficients (K) are similar for bacteria and seston and independent of Aroclor. The similarity in values for 1016 and 1242 is reasonable because the properties of these mixtures are so similar. The extent of sorption of the Aroclors to seston is only slightly lower than sorption to the bottom sediments[14]. Although the data are not reported here, sorption of Aroclors to seston and bacteria indicate that the values of partition coefficients for early eluting isomers (dichlorobiphenyls) are about one-half the value for the later eluting isomers (tetra-, penta-, and hexachlorobiphenyls).

Water-octanol partition coefficients for Aroclors 1016 and 1242 are included because partition coefficients between organic solvents and water are widely

used as an indicator of bioaccumulation potential. Values for the partition coefficients between octanol and water are an order of magnitude higher than partition coefficients for bacteria and seston. Partitioning of individual components between octanol and water was similar to the behavior with seston and bacteria, that is, the extent of sorption was inversely related to the extent of chlorination of the isomers.

Table 1. Partition coefficients (K) of Aroclors 1016 and 1242.

Seston, sediment, or bacteria	K_{1016}*	K_{1242}*
Doe Run Pond bacteria	$(6.3\pm1.4) \times 10^3$	$(8.3\pm3.2) \times 10^3$
Hickory Hills Pond bacteria	$(6.4\pm0.8) \times 10^3$	$(4.5\pm1.5) \times 10^3$
USDA pond bacteria	$(5.5\pm2.9) \times 10^3$	$(2.9\pm1.8) \times 10^3$
Doe Run Pond seston	$(2.0\pm1.1) \times 10^3$	$(5.3\pm2.1) \times 10^3$
Hickory Hills Pond seston	$(2.5\pm1.1) \times 10^3$	$(4.7\pm2.4) \times 10^3$
USDA pond seston	$(1.2\pm0.7) \times 10^3$	$(2.2\pm1.4) \times 10^3$
Doe Run Pond sediment†	$(1.29\pm0.8) \times 10^3$	$(1.09\pm.16) \times 10^3$
Hickory Hills Pond sediment†	$(1.30\pm.09) \times 10^3$	$(1.25\pm.11) \times 10^3$
USDA pond sediment†	$(1.37\pm.14) \times 10^3$	$(1.21\pm.12) \times 10^3$
Octanol-water	$(2.4\pm1.4) \times 10^5$	$(1.3\pm0.8) \times 10^5$

*Mean of six determinations.

†Steen et al.[14]

From the values of the partition coefficients between water and seston (Table 1), it is evident that the concentration of hydrophobic compounds measured in natural waters can be strongly influenced by the extent of sorption. Disregarding bottom sediment influence, the effect of seston on the observed total concentration in the water column can be described by:

$$C_{TOT} = \frac{KM}{W} C_{DISS} + C_{DISS} \qquad (2)$$

where: C_{TOT} = dissolved and sorbed concentrations of Aroclor

C_{DISS} = dissolved concentration of Aroclor

M = mass of seston

W = mass of water

Thus, the fraction of 1242 or 1016 associated with seston increases as the mass of seston increases. For example, at very low concentrations of seston, such as 10 mg/l, the Aroclor in the water column would be mostly in solution and the effect of seston would not be significant. At 300 mg/l of seston, however, the total concentration would be twice that of the dissolved concentration. To check this point, we introduced 1242 into filtered (0.22 μ filter) and non-filtered pond water by equilibration with the vapor phase. The unfiltered

sample with 83 mg/l of seston contained 33% more 1242 than the filtered water. This is within 12% of the calculated values.

Volatilization

Laboratory studies by Oloffs et al.[15] have shown that Aroclor 1260, a polychlorinated biphenyl mixture, is lost to the atmosphere through volatilization from water. Also, significant concentrations (3-9 ng/m^3) of Aroclor 1254 were found in air samples collected near Baltimore, MD, during an Upper Chesapeake Bay study[16]. These studies and others[5,17] indicate vapor phase transport can be a significant pathway for loss of PCB's from water bodies. Two models have been used to estimate pollutant volatilization rates from water[18-19].

Mackay and Leinonen's[18] model requires a knowledge of the Henry's law constant value (H) and approximate values of vapor and liquid mass transfer coefficients. Values of Henry's law constants for 1016 and 1242 were found to be 5.7 ($\pm$ 3.0) x 10^{-5} and 3.2 ($\pm$ 1.9) x 10^{-5}, respectively. (Units of vapor concentrations and aqueous concentrations were mm Hg and mole fractions, respectively.) No significant difference between H values for saturated and more dilute solutions was found. Using these values of H in Mackay and Leinonen's model, the half-life of 1016 in a column of water, 1 square meter surface area and 1 meter deep, would be 9.9 hours; the half-life of 1242 would be 11.2 h. These half-lives, however, do not take into consideration degradation, sorption, or turbulence.

The rate of loss of volatile materials from water is strongly influenced by the turbulence of the system. Because turbulence is difficult to quantify on an absolute basis, however, the rate of volatilization cannot be determined as a function of turbulence. Fortunately, the ratio of the rate coefficients for reaeration (k_2) and PCB loss (k) are independent of turbulence[20]. Gas exchange experiments were, therefore, undertaken to determine these first order rate coefficients[19].

Concentrations of oxygen and PCB for each replicate were used to determine the values of k and k_2 at the three mixing speeds. The ratios of k to k_2 were computed for each beaker and averaged for each mixing speed. As shown in Table 2, the ratios were not affected by the degree of turbulence.

Table 2. Ratios of oxygen reaeration rate coefficients (k_2) to Aroclor volatilization rate coefficients (k) at three stirring speeds.

Vortex depth (cm)	Aroclor 1016* (k/k_2)	Aroclor 1242* (k/k_2)
2	.26 ± .03	.23 ± .04
4	.23 ± .05	.23 ± .04
9	.27 ± .05	.19 ± .03

*Mean of eight determinations.

Tsivoglou et al.[20] showed that, for simultaneous transfer of pairs of gases, the ratio of gas exchange coefficients can be estimated as the reciprocal of the ratio of molecular diameters. Although Aroclors are neither gases nor spherical molecules, the ratio of k and k_2 was estimated from this procedure and compared with our laboratory values. Two different values for the polychlorinated biphenyl diameter were obtained depending on the method of estimation used.

Using the Lorenz-Lorentz equation[21], a molecular diameter of 5.92 Å was estimated, but measurement with a Dryden model of 4,4'-dichlorobiphenyl gave a value of 10.6 Å. Using 2.95 Å for the molecular diameter of oxygen[22], the ratio of rate coefficients is 0.5 with the former value for PCB molecular diameter and 0.28 with the latter. The latter ratio agrees very well with the experimentally determined value.

Thus far, Aroclor volatilization from seston-free water has been considered. Disregarding the sediments, the rate of volatilization from a water column is affected by partitioning of 1016 or 1242 to the seston. Partitioning to seston lowers the Aroclor concentration in solution and thereby lowers the Aroclor volatilization rate. The relationship of Aroclor volatilization and partitioning is shown in the following equation.

$$-\frac{dC_{TOT}}{dt} = \frac{k}{1 + KM/W} C_{TOT} \qquad (3)$$

Experimental ratios of oxygen reaeration rate coefficients to Aroclor volatilization rate coefficients are compiled in Table 3 with values calculated from equation 3. Calculated and experimental ratios are in good agreement.

Table 3. Volatilization - sorption for Aroclor 1242

Site	Dry weight of seston	Calculated (k/k_2)	Experimental* (k/k_2)
Doe Run Pond	83.1 mg/l	.16	.14 - .16
Hickory Hills Pond	95.1 mg/l	.16	.12 - .15
USDA pond	144.4 mg/l	.17	.15 - .19

*Results of two determinations.

CONCLUSIONS

Because of the low apparent water solubility of Aroclors 1016 and 1242, the dissolved concentrations of these mixtures in the aquatic environment would be expected to be low. When not highly sorbed to sediments, volatilization would be a significant transport pathway; whereas when highly sorbed, these Aroclors would be transported in association with seston within the aquatic environment. For total assessment of the behavior of polychlorinated biphenyls in the aquatic environment, concentrations of both dissolved and sorbed fractions need to be determined.

ACKNOWLEDGMENTS

We wish to thank Dr. R. G. Webb for his gifts of Aroclor 1016 and 1242, Drs. D. S. Brown and J. W. Falco for their helpful discussions, and J. T. Barnett, H. W. Maca, and M. R. Miles for their technical assistance.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

1. H. J. Crump-Weisner, H. R. Feltz, and M. L. Yates, Pesticide Monitoring J., 8, 157-161 (1974).

2. "Proceedings of National Conference on Polychlorinated Biphenyls." U.S. Environmental Protection Agency Report #EPA-560/6-75-004 (1976).

3. R. G. Webb and A. C. McCall, J. Chromatographic Sci., 11, 366-373 (1973).

4. E. S. Tucker, W. J. Litschqi, and W. M. Mees, Bull. Environ. Contamin. Toxic., 13, 86-94 (1975).

5. I. C. T. Nisbet and A. F. Sarofim, Environ. Health Persp., 21-38 (1972).

6. D. Mackay and A. W. Wolkoff, Environ. Sci. Technol., 7, 611-614 (1973).

7. B. T. Johnson and J. O. Kennedy, Appl. Microbiol., 26, 66-71 (1973).

8. G. S. Sayler and R. R. Colwell, Environ. Sci. Technol., 10, 1142-1147 (1976).

9. G. Eder, Chemosphere, 2, 101-106 (1976).

10. D. F. Paris and D. L. Lewis, Bull. Environ. Contam. Toxic., 15, 24-32 (1976).

11. D. F. Paris, D. L. Lewis, and J. T. Barnett, Bull. Environ. Contam. Toxic., 17, 564-572 (1977).

12. R. Haque, D. W. Schmedding, and V. H. Freed, Environ. Sci. Technol., 8, 139-142 (1974).

13. C. P. Rice and H. C. Sikka, J. Agr. Food Chem., 21, 148-152 (1973).

14. W. C. Steen, D. F. Paris, and G. L. Baughman, Water Res. (In press).

15. P. C. Oloffs, L. J. Albright, and S. Y. Szeto, Canadian J. of Microbiology, 18, 1393-1398 (1972).

16. T. O. Munson, D. K. Ela, and C. Rutledge, Jr., "Upper Bay Survey, Final Report to the Maryland Dept. of Natural Resources, Vol. II," Westinghouse Electric Corp., Annapolis, MD (1975).

17. V. E. McClure, Environ. Sci. Technol., 10, 1223-1228 (1976).

18. D. Mackay and P. J. Leinonen, Environ. Sci. Technol., 9, 1178-1180 (1975).

19. J. Hill IV, H. P. Kollig, D. F. Paris, N. L. Wolfe, and R. G. Zepp, "Dynamic Behavior of Vinyl Chloride in Aquatic Ecosystems," U.S. Environmental Protection Agency Report #EPA-600/3-76-001 (1976).

20. E. C. Tsivoglou, "Tracer Measurement of Stream Reaeration," Federal Water Pollution Control Administration, U.S. Department of Interior (1967).

21. W. J. Moore, "Physical Chemistry," Prentice Hall, Inc., New York, NY, 1963, p. 561.

22. R. C. Weast, "Handbook of Chemistry and Physics," 53rd edn., The Chemical Rubber Co., Cleveland, OH, 1973, p. F-191.